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STABILITY AND EMITTANCE OF

MOLYBDENUM DISILICIDE COATING

UNDER VARYING TEMPERATURES AND PRESSURES

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STABILITY AND EMITTANCE OF
MOLYBDENUM DISILICIDE COATING
UNDER VARYING TEMPERATURES AND PRESSURES

Contract AF 33(657)-8706

Project 281

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THE Marquardt CORPORATION
VAN NUYS, CALIFORNIA

TABLES

ILLUSTRATIONS

ACKNOWLEDGMENTS

The work reported herein was performed in the Materials and Process Laboratory of The Marquardt Corporation at Van Nuys, California. The tests were made by R. W. Titus, Jr. and R. M. Davids. Compilation of data and analyses were made by S. I. Bocarsly. The contributions to this report by the above-named personnel are acknowledged.

I. SUMMARY

Temperature and Pressures

A test program was conducted to study the effect of both low pressure and temperature on disilicide coated 0.5% titanium-molybdenum alloy. The specific properties studied were the loss of surface coating by evaporation and the effect on surface emittance of this evaporation at the operational temperatures of a rocket engine system.

It was found that the Langmuir equation for evaporation rates is applicable, and that the rate of evaporation was such that only minor amounts of coating would evaporate during the system duty cycle. It was also found that essentially no change in emittance occurs due to this evaporation.

Emittance

Various methods of preparing the metal substrate surface were investigated. Of these, grit blasting increased the emittance of the bare molybdenum surface over that of the disilicide coated surface.

II. INTRODUCTION

The radiation cooled combustion chamber referred to in this report (See Figure 1) was fabricated from 0.5% Ti-molybdenum alloy. A disilicide coating was applied for oxidation protection using the pack cementation process. This protection was necessary because the combustion chamber is an integral part of a radiation-cooled rocket engine system. In this system, the rate of heat transfer (wall temperature) for the combustion chamber is governed by the emittance of the outer surface. The system studied must operate at an altitude of at least 1,000 miles, where it is expected that the pressure levels will be no higher than 10^{-10} mm of mercury. Wall temperatures under steady state operation are expected to be in the area of 2800° to 3000°F, based on the measured emittance of the disilicide coated surface.

Oxidation protection of the combustion chamber interior is necessary because the combustion products of the propellant system used contain large amounts of water vapor and other oxidizing gases. Oxidation protection of the exterior surfaces of the combustion chamber is not necessary because of the nonoxidizing environment of space. The coating does, however, provide a significantly higher emittance than the base metal which results in a lower wall temperature. Wall temperatures should be kept below 3000°F because the reliability of the oxidation protection coating on the interior surfaces becomes questionable above this temperature.

During space simulation testing of disilicide coated combustion chambers in the Marquardt laboratory, it was noted that silicon was deposited on adjacent cold surfaces. It was determined that this resulted from evaporation of the disilicide coating which is composed essentially of silicon compounds of molybdenum. Although this would not affect the combustion chamber from an oxidation protection standpoint, it would cause higher wall temperatures. The coating loss

would expose areas of bare molybdenum metal, causing lower emittance and resulting in an increased wall temperature. This, in turn, would increase the evaporation rate of the coating and would ultimately lead to catastrophic oxidation on the interior surfaces of the combustion chamber. Also, the evaporated silicon would deposit on all cold surfaces and might affect the efficiency of other components of the rocket engine system.

This report describes a test program that was conducted to determine the evaporation rate of the molybdenum disilicide coating at operating temperatures, the effect of this evaporation on the emittance of the exposed surfaces, and the effect on the emittance of surface roughening by grit blasting.

III. EXPERIMENTAL TECHNIQUES

A. Evaporation and Emittance Change Studies

Analytical studies were made to determine the effect of temperature and low pressure on the molybdenum disilicide coating. The Langmuir equation for evaporation rate was used in these studies to construct the plot of vapor pressure and temperature relationship shown in Figure 2.

Test specimens were prepared as follows:

Samples of 0.5% Ti-molybdenum alloy sheet and bar were fabricated to the configuration in Figure 3. Surface finishes duplicated those specified on the combustion chamber drawing. The specimens were then disilicide coated 0.0015 to 0.003 inch thick. After coating, the specimens were oxidation tested to determine the integrity of the coating and they were dimensionally inspected (See Table I). The coating was stripped in hydrofluoric acid for 3/4 inches on each end to provide good electrical contact.

An area approximately 1/4 by 1/4 inch was grit blasted at the center of each specimen to provide a zone for thermocouple attachment. This area also served for determining the effect of grit blasting on emittance.

The specimens were then solvent cleaned and thermocouples were spot welded to the grit blasted zone.

Finally, the specimens were dried by heating to 250°F for 1 hour and weighed while warm (See Table II) after which they were placed in a desicator until tested.

The test procedures were as follows:

1. Place the specimen between the electrodes (See Figure 4).

2. Connect the thermocouple to the leads.

3. Place the bell jar in position.

4. Evacuate the system to obtain the test pressure.

5. Heat the specimen to the test temperature

6. Measure the temperature at stated intervals using thermocouples and a micro-optical pyrometer.

7. After the specified test time, cool the specimen to room temperature, maintaining the test pressure.

8. Remove the specimen from the electrode saddle and weigh it immediately.

9. Measure the thickness of specimen.

The test results are shown graphically in Figures 5 through 7.

B. Effect of Grit Blasting on Emittance

The disilicide coated radiation cooled combustion chamber (See Figure 1) previously discussed was investigated to determine the effect of grit blasting on the emittance of the molybdenum disilicide coated surface. The outside surface of the combustion chamber was blasted with Carborundum 20RA silicon carbide grit. Air pressures used were 20, 40, 45, and 60 psi. The chamber was then heated to 1800°F using induction heating equipment and emittance measurements were made.

The bell section of the combustion chamber was then abrasive cut from the combustion chamber and emittance was measured on both the grit blasted surface (outside) and the disilicide coated surface (inside).

Emittance measurements were made at approximately 2500° and 2800°F, using the equipment shown in Figure 4. Heating was accomplished by self-resistance and true temperature measurements were made with a platinum-platinum/13% rhodium thermocouple. A Leeds and Northrup Model 8663 potentiometer was used to measure the emf. Indicated temperatures were measured with a micro-optical pyrometer. The tests were performed in an argon atmosphere. The results of these tests are presented in Table III.

IV. RESULTS AND DISCUSSION

A. Evaporation Studies

During altitude firing of rocket motors, silicon deposits were noted on cold elements of the system. Since this could occur only by evaporation, a study was made to determine the mechanism.

Langmuir determined that evaporation was a function of pressure and temperature. Also, he showed that once the pressure level of a system was below the vapor pressure, then lowering the pressure still further was not nearly as rate controlling as temperature. The major function of lowering the pressure was to increase the mean free path of the atoms or molecules leaving the surface.

It was shown by other (Vacuum Techniques - Dushman) that, in a laboratory system, hard vacuum could be simulated by having a large vacuum pump opening with respect to the sample. This condition would effectively limit the number of collisions between atoms and/or molecules leaving the surface which result in random returns to the surface, by removing them from the system. It was further stated that a pressure level of 10^{-5} mm of Hg in such a system was sufficient to simulate near zero pressure effects on a material.

A theoretical calculation of the evaporation rate of the disilicide coating was performed using the following relationship determined by Langmuir:

$$W = \frac{P}{17.14} \sqrt{\frac{M}{T}}$$

Where

W = Rate of evaporation, grams/sq cm/sec

P = Vapor pressure, mm Hg

M = Molecular weight of the material

T = Temperature, °K

It is obvious from this relationship that the molecular weight of the evaporating material must be known. Although the disilicide coating was known to be basically a silicon molybdenum reacted layer, the exact chemistry of the system was not known. Therefore, it was assumed that the outer surface was all silicon and a thinner boundary layer was all molybdenum (minor alloying elements were disregarded).

A vapor pressure versus temperature curve was then constructed (Figure 2) with the silicon and molybdenum curves representing the limits. Vapor pressures for various compounds of silicon and molybdenum, chosen at random, were then constructed. Based on this information, the weight loss curve, Figure 5, was constructed.

Since the rate of loss of coating was then assumed to be in this envelope, but the limits were several orders of magnitude different, a test program was conducted to determine where the disilicide coating system would fit in the family of calculated curves.

The test results are shown in the broken line of Figure 5, indicating that the effective analysis of the coating approaches that of $Mo_5 Si_3$. The effective molecular weight and vapor pressure can also be determined from this plot.

The coated specimens used in this test program were prepared from both sheet and bar, with no noticeable difference being observed in the coating. This was as expected since the coating depends on the chemistry of the system and not on prior working of the metal. No attempt was made to analyze the mode of evaporation. Profilometer readings indicated that a general improvement in surface finish had occurred. Dimensional check of the samples indicated that the thickness, as expected, had decreased at the lower pressure level (Figure 6). The thickness increased during exposure to relatively higher pressures, which was to be expected because of the complex reactions of the surface silicon and atmosphere contaminants.

B. Emittance Change Studies

Another objective of the test program was to study the change in emittance under the vacuum condition. If the coating did evaporate or change substantially, chemically or dimensionally, a change in the emittance of the exposed surface would be expected.

Emittance measurements were made during each test sample run and essentially no change was noted, as shown in Figure 7, for the run time. This result tends to substantiate the belief that the rate of change of surface exposed is slow compared to the operational life of the rocket engine system. Therefore, the changes that do occur are not significant.

A check was made on the grit blasted zone of the test samples. The emittance values obtained substantiated the original values obtained for the grit blasted combustion chamber, indicating that there had been no change in emittance.

C. Grit Blast Tests

Emittance measurements which were made on disilicide coated 1/2% Ti-molybdenum alloy were found to be in the range of 0.62 to 0.72. This value has been confirmed in numerous other tests made by The Marquardt Corporation.

Based on the discoveries of Mendenhall, namely, that a 10° wedge could approximate a black body in metallic surfaces, it was deduced that any random surface roughening would probably increase the emissivity over that of the smooth metallic surface.

Since the only function of the disilicide coating on the outside surface of the combustion chamber was to increase the emittance over that of the bare metal, removal of the coating for another type of high emittance surface was feasible.

A combustion chamber was grit blasted, with nominal 20 mesh silicon carbide (the grit size analysis is given in Table IV.) It was found that a minimum pressure of 45 psi was necessary to remove the coating. A second sample was blasted at 60 psi to determine the effects of additional roughening. It was found that the surface which was grit blasted at the lower pressure did not have a significantly higher emittance than the coated surface. However, the emittance of the

surface which was grit blasted at 60 psi was found to have increased to 0.8 to 0.85. Substantiation of the increase was confirmed by retaining the disilicide coating on one side of the sample, and measuring it during the same measurement setup. The emittance of this disilicide coated side was found to be 0.62 to 0.72.

V. CONCLUSIONS

Based on the work performed, the following conclusions were derived:

1. The emittance of the 0.5% Ti-molybdenum alloy combustion chamber can be increased by controlled grit blasting of the surface.

2. The coating evaporation rate would not be significant for the operational life of the rocket engine system which was studied.

3. Emittance did not change significantly during the 32-minute exposure to conditions of low pressure and temperature.

4. Samples of bar stock and sheet stock showed no significant difference in test results.

5. The Langmuir equation predicts evaporation rates adequately and, therefore, evaporation rate tests need not be conducted on a material of known molecular weight and vapor pressure.

TABLE I

THICKNESS AND SURFACE FINISH OF DISILICIDE COATED
0.5% Ti-MOLYBDENUM EMITTANCE TEST SPECIMENS AFTER COATING

Specimen No.	Measurement Through Center Section			Surface Finish (rms)		
	After Coating		Thickness After Test (in.)	After Coating		After Test (Average)
	Width (in.)	Thickness (in.)		One Side	Opposite Side	
1	0.7660	0.0419	0.0419	70 to 80	50 to 60	35
2	0.7517	0.0470	0.0469	84 to 98	50 to 75	40
3	0.7420	0.0432	0.0431	100 to 120	50 to 60	42
4	0.7665	0.0413	0.0411	60-	70 to 75	36
5	0.7355	0.0410	0.0405	60-	80-	48
6	0.7663	0.0423	0.0422	60-	70 to 160	35

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TABLE II

WEIGHT CHANGE PER UNIT AREA AFTER EXPOSURE

Specimen No.	History of Sample	Weight Change per Unit Area (Each Test) (grams/sq cm)	Combined Weight Change per Unit Area (grams/sq cm)
1	Sheet: 10 min at 2800°F, 1000 mm 32 min at 2800°F, 2 mm	0.0052 0.0215	0.0267
2	Bar: 10 min at 2800°F, 1000 mm 32 min at 2800°F, 2 mm	0.0047 0.0198	0.0245
4	Sheet: 10 min at 2800°F, 1000 mm 32 min at 2800°F, 2 mm		0.0254
7	Sheet: 10 min at 2800°F, 1000 mm	0.0042	0.0042
3	Bar: 32 min at 2500°F, 2 mm	0.0046	0.0046
6	Sheet: 32 min at 2500°F, 2 mm	0.0037	0.0037
5	Sheet: 32 min at 3000°F, 2 mm	0.0691	0.0691

TABLE III

EMITTANCE OF GRIT BLASTED AND DISILICIDE COATED 0.5% Ti-MOLYBDENUM ALLOY

Surface Condition (Bell Section)	True Temperature Pt/Pt-13% Rh T.C. (°F)	Micro-optical Temperature 0.65 Angstoms (°F)	Emittance
Disilicide Coated	2652	2580	0.72
	2735	2650	0.70
	2860	2760	0.70
Grit Blasted, 45 psi	2450	2395	0.75
	2785	2710	0.76
60 psi	2170	2140	0.83
	2630	2590	0.84
	2850	2805	0.84
Combustion Chamber LRL Induction Head	1800	1775	0.85

TABLE IV

GRIT SIZE ANALYSIS

Grit Size	%
20	14.3
20 to 35	29.6
35 to 50	19.3
50 to 80	14.6
80 to 100	6.9
100 to 140	7.5
140 +	7.8

Material = Carborundum 20 RA Silicon Carbide

DIAGRAM OF A RADIATION COOLED COMBUSTION CHAMBER

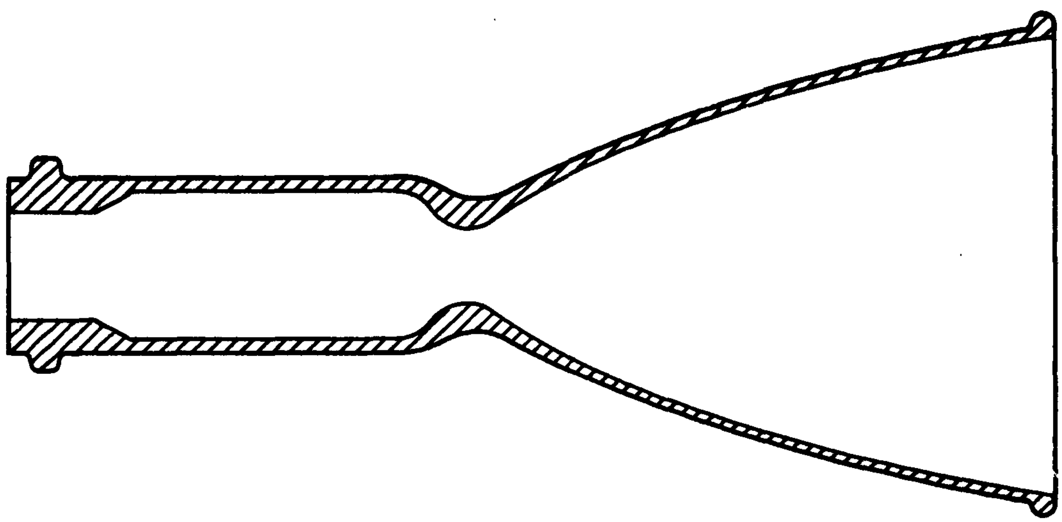
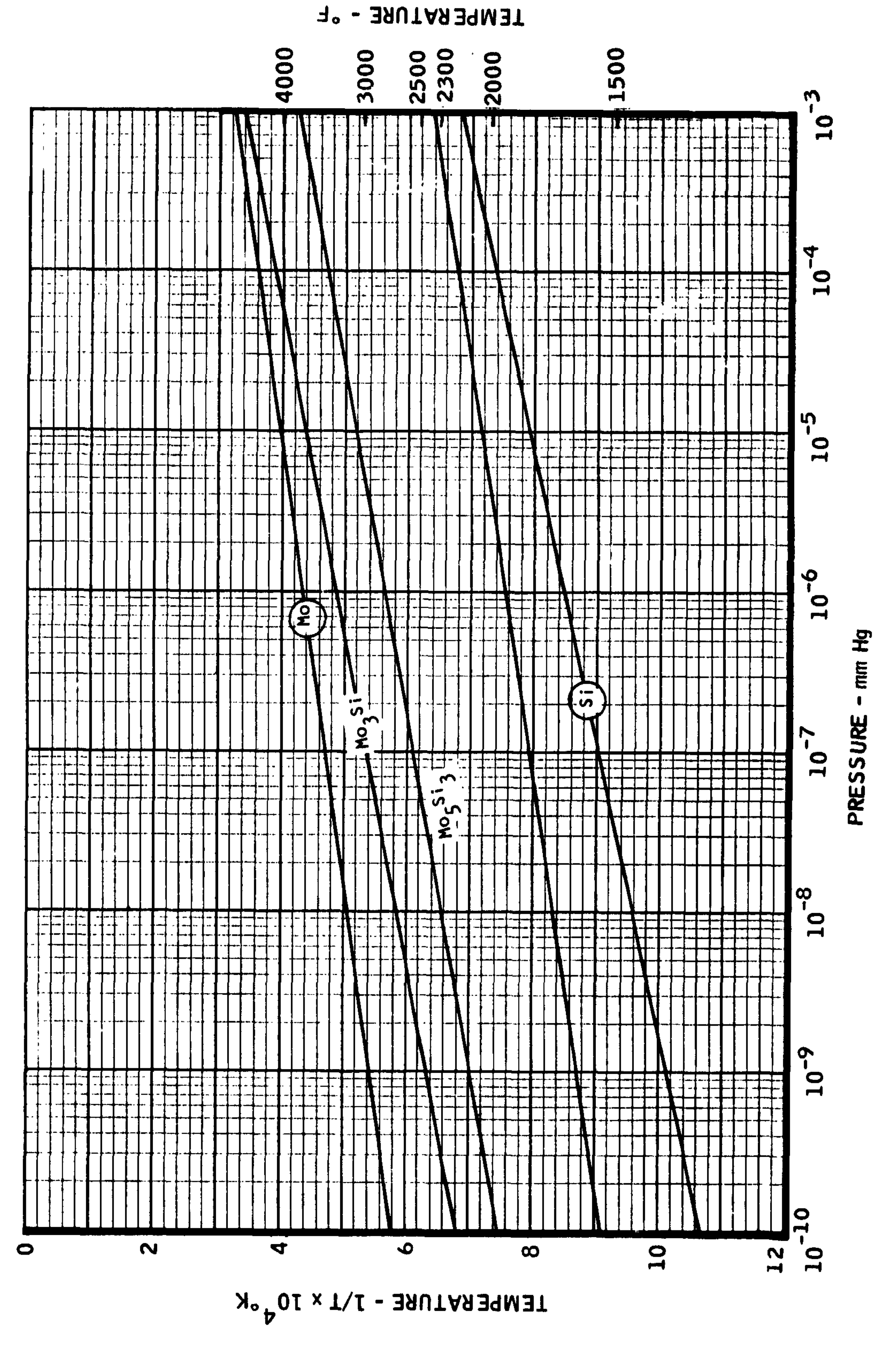
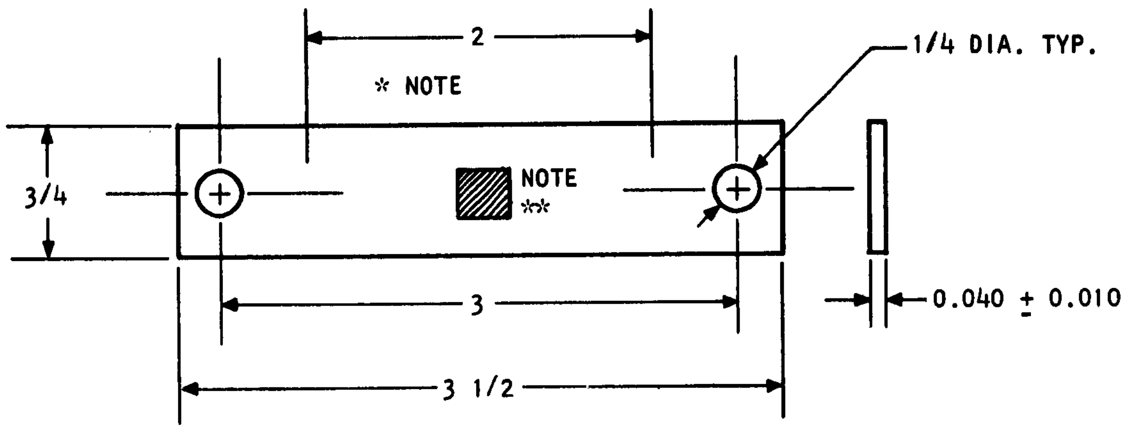


FIGURE 1

VAPOR PRESSURE - TEMPERATURE RELATIONSHIP FOR MOLYBDENUM AND SILICON COMPOUNDS



TEST SPECIMEN CONFIGURATION USED FOR DISILICIDE COATING TESTS



NOTES:

* SURFACE FINISH IN THIS AREA = 60 to 65 RMS FOR ALL SPECIMENS
** GRIT BLASTED ZONE USED FOR THERMOCOUPLE ATTACHMENT
ALL DIMENSIONS IN INCHES

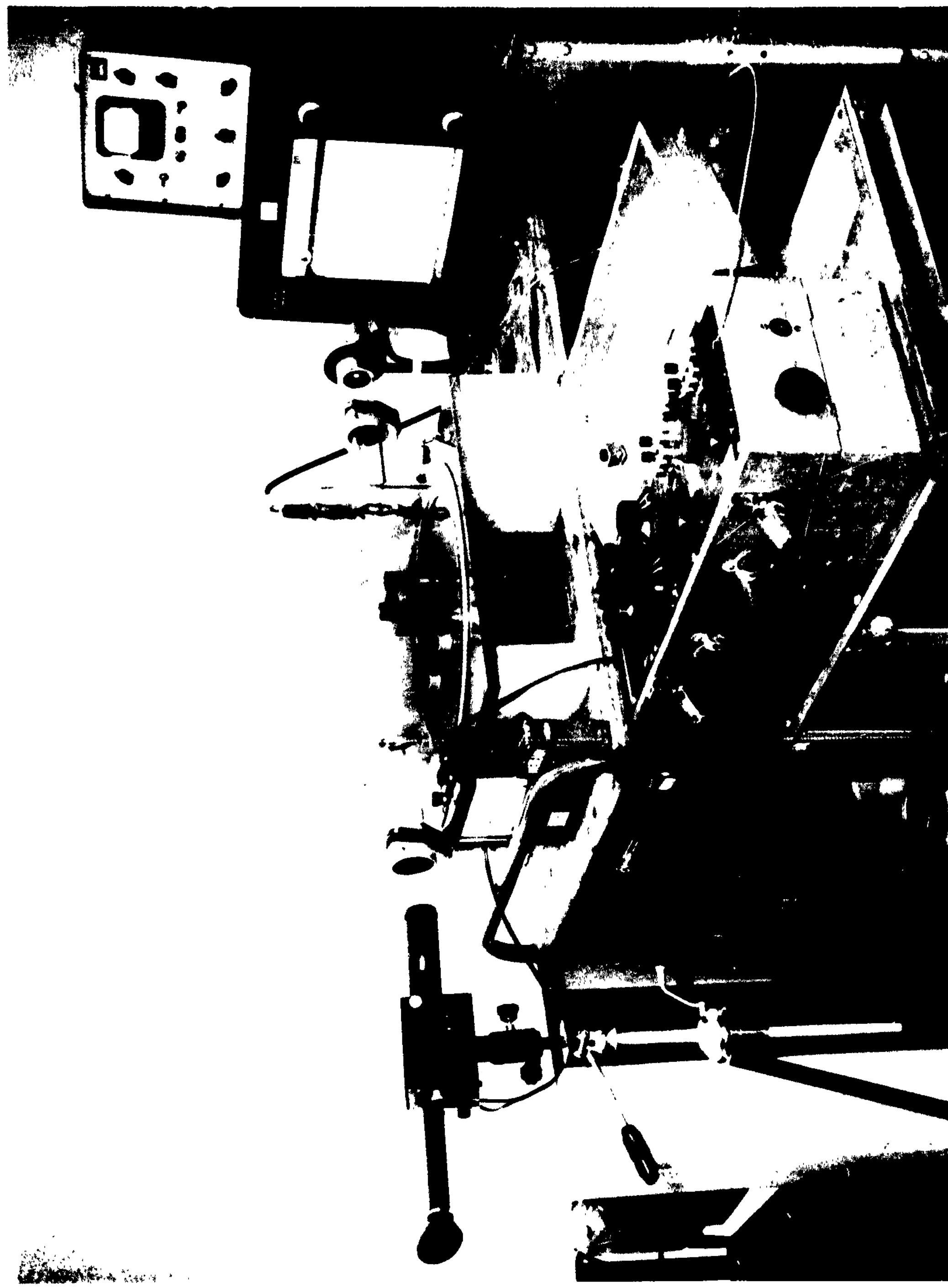


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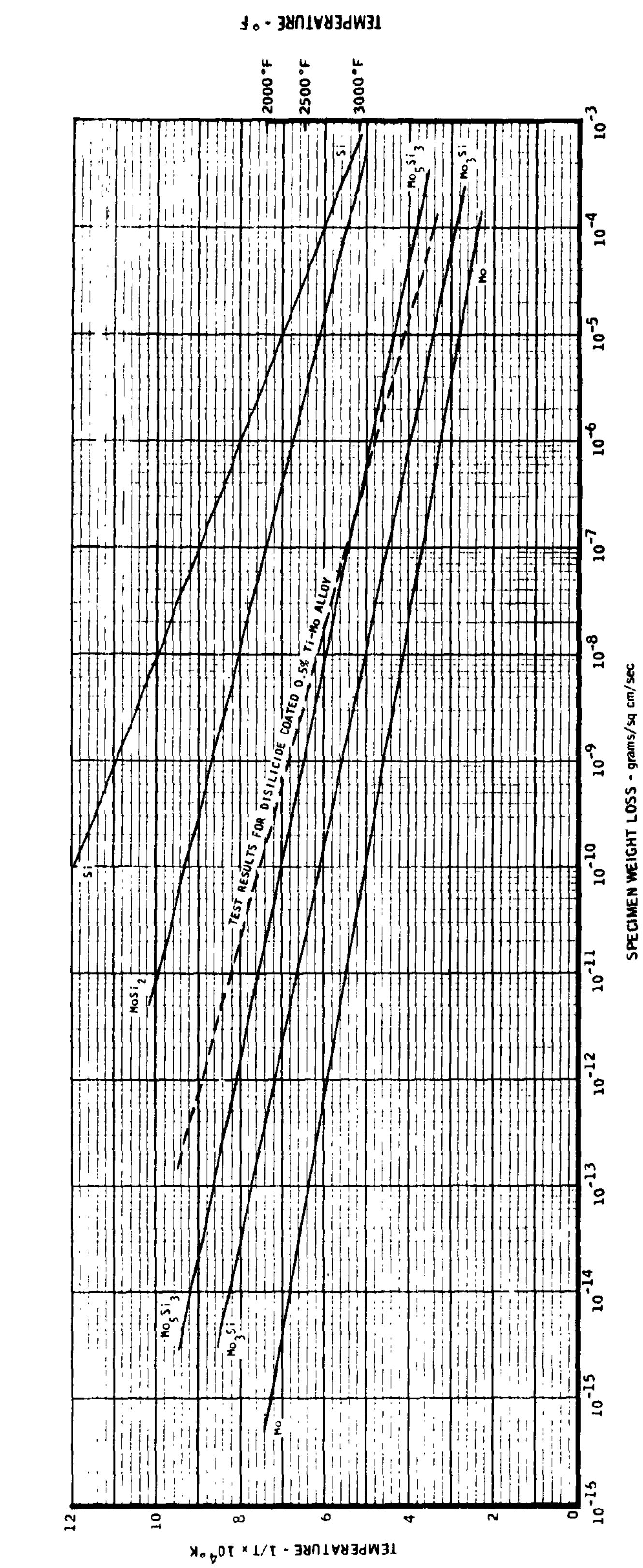
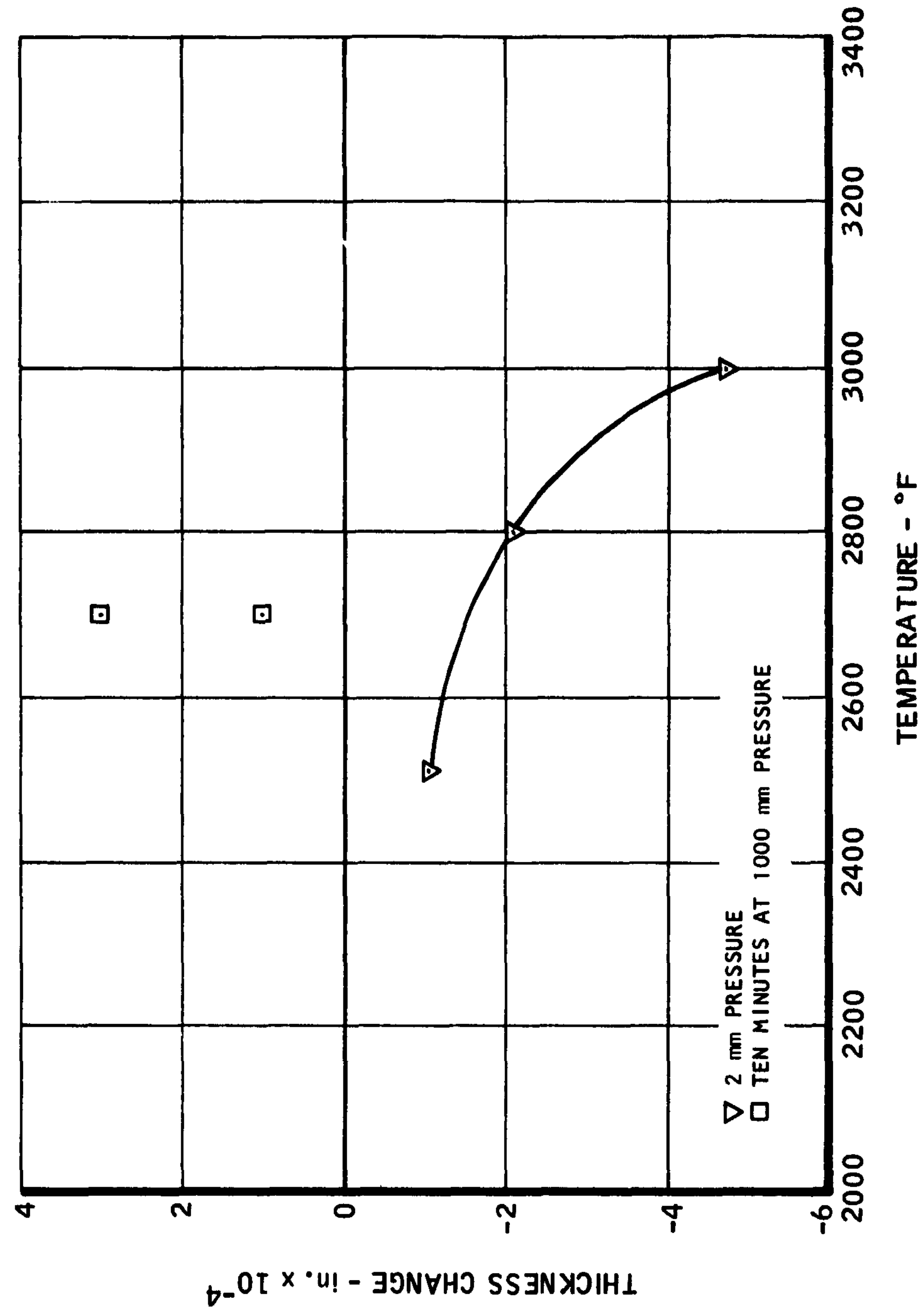
FIGURE 4 - Apparatus Used for Measuring Emittance

WEIGHT LOSS vs. TEMPERATURE FOR MOLYBDENUM AND SILICIDE COATINGS



TOTAL SIZE CHANGE OF DISILICIDE COATINGS
AFTER 32 MINUTES AT VARIOUS TEMPERATURES AND PRESSURES



VARIATION OF EMITTANCE OF DISILICIDE COATED AND GRIT BLASTED MOLYBDENUM ALLOY SPECIMENS WITH TIME AT 2800° F

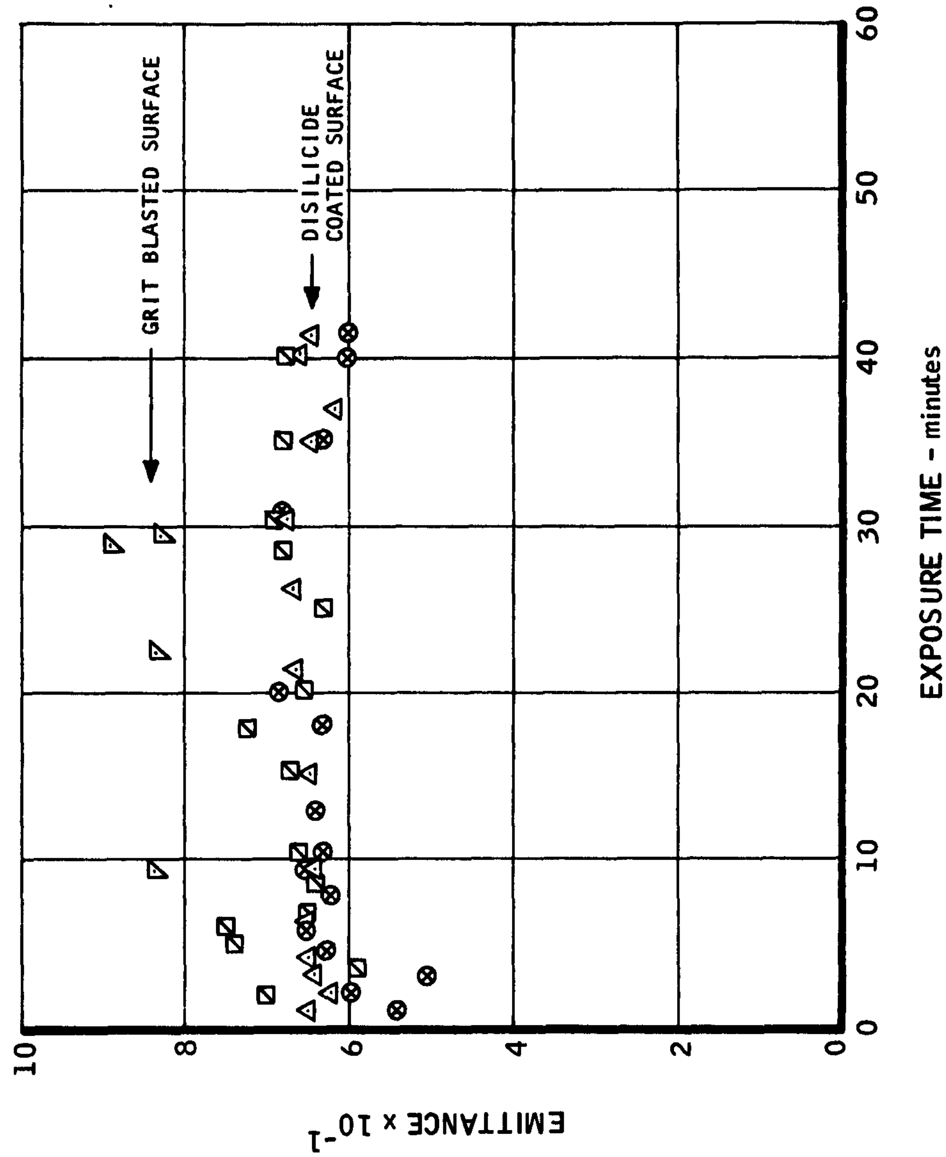


FIGURE 7

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